

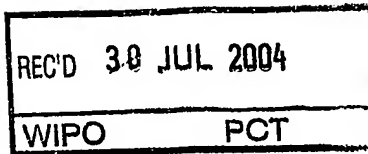


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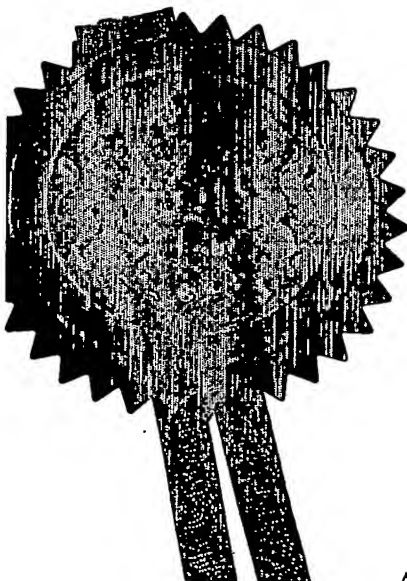


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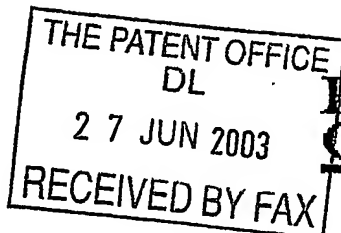
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K.U.Leuven Research and Development - Groot Begijnhof 59 - 3000 Leuven

Represented by Dr. Ivo Roelants, IPR Officer

Patents ADP number (if you know it)

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7665649003

4. Title of the invention

Zeotiles

5. Name of your agent (if you have one)

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ZEOTILES

FIELD OF THE INVENTION

The present invention relates a new class of crystalline silica, said materials having two levels of porosity and structural order.

BACKGROUND OF THE INVENTION

Silica molecular sieves with controlled porosity crystallise from hydrogel in the presence of organic template molecules.¹ Patterned, mesoporous silica materials with amorphous walls are obtained using structure directing surfactants² or blockpolymers³. In diatoms and sponges the formation of macroporous silica structures is directed by biopolymers and proteins.⁴

The generation of zeolite properties such as acidity and hydrothermal stability in mesostructured materials is a lively research field. The possibility to transform part of the amorphous walls of a mesoporous precursor into zeolite framework was demonstrated,⁵ but segregation of a zeolite phase from the mesostructure as conversion proceeds seems difficult to avoid.^{7,8} A more direct way to embed zeolite fragments in walls separating mesopores is by assembling the mesophase from suspensions containing zeolite crystallisation nuclei.⁹⁻¹² The obtained materials invariably have hexagonal symmetry and contain undefined zeolite fragments. We deliberately synthesised nanometer size building units having zeolite framework and assembled them in various ways into mesoporous phases.

SUMMARY OF THE INVENTION

The present invention describe a new class of crystalline silica materials, said materials having two levels of porosity and structural order. At the first level, building

units are nanoslabs of uniform size having the Silicalite-1 zeolite framework generated by the tetrapropylammonium template.⁶ At the second structural level, nanoslabs are linked through their corners, edges or faces following patterns imposed by interaction with cationic surfactant or triblock copolymer molecules. After evacuation of the organic molecules, microporosity is obtained *inside* the nanoslabs, and a precise mesoporosity *between* the nanoslabs depending on the tiling pattern of the zeolite slabs. Therefore, the use of cationic surfactants (preferably quaternary ammonium salts) or triblock copolymer molecules in order to impose an organisation to the nanoslabs is a second object of the invention. In a first embodiment four different tiling patterns were prepared and directly imaged by electron microscopy. X-ray diffraction confirms the mosaic structures derived from electron microscopy. Application fields are catalysis and molecular separation, adsorption of metal ions, fixation of biologically active species, electro-optical and dielectric materials.

LIST OF FIGURES

Figure 1. Sample A. XRD pattern (a) and HREM micrograph (scale bar = 10 nm) with Fourier transform insert (b) of Zeotile-1. The XRD pattern is indexed according to the hexagonal tiling of nanoslabs ($2.6 \times 2.0 \times 4.0 \text{ nm}^3$) as shown on the HREM image (blue rectangles).

Figure 2. Sample B. XRD pattern of Sample B (a) and HREM images with FT inserts of Zeotile-2 (b) and Zeotile-3 (c) (scale bars = 10 nm). The XRD pattern has been indexed according to the tiling of the prominent Zeotile-2 phase (vertical lines). The presence of Zeotile-1 is evident from XRD (corresponding reflections are marked with stars). No direct evidence for Zeotile-3 is derived from XRD due to its low amount. The tiling patterns of Zeotile-2 and -3 are schematically represented on the HREM images with blue rectangles ($2.6 \times 2.0 \text{ nm}^2$ for Zeotile-2 and $1.3 \times 2.0 \text{ nm}^2$ for Zeotile-3).

Figure 3. Sample C. HREM image with electron diffraction pattern insert of Zeotile-4 (scale bar = 20 nm).

ILLUSTRATIVE EMBODIMENT

Nanoslabs with the well known Silicalite-1 structure type¹³ are prepared through hydrolysis of tetraethylorthosilicate (TEOS) in concentrated solution of tetrapropylammonium hydroxide (TPAOH).⁸ Silicalite-1 nanoslab formation is directed by TPA cations. The nanoslab size is controlled by the synthesis conditions.⁵ Sample A preparation departs from a basic suspension of nanoslabs with dimensions of $1.3 \times 2.0 \times 4.0 \text{ nm}^3$. Aggregation of these nanoslabs into an open structure is achieved by addition of an aqueous solution of cetyltrimethylammonium bromide (CTAB), a surfactant known to favour formation of uniform mesoporous channel structures.² In the Sample B preparation, CTAB is added in powder form. The organics are removed from the solid product obtained through oxidation and leaching with ethanolic nitric acid solution. Powder X-ray diffraction (XRD) and high-resolution electron microscopy (HREM) are used to characterise the obtained superstructures. In HREM, a low intensity electron beam and medium magnifications are used to minimise electron beam damage of the structure. The HREM images are taken in overfocus conditions where the image directly represents the structure; the bright dots correspond to the projection of the channels. On the HREM images the schematic, projected mosaic structure is superimposed.

A first superstructure, referred to as Zeotile-1, is present in Sample A (Fig.1). In Zeotile-1, nanoslabs are forced into face sharing, double nanoslab units, measuring $2.8 \times 2.0 \times 4.0 \text{ nm}^3$ and linked in a hexagonal symmetry pattern (Fig.1). XRD confirms the phase purity (Fig.1). A mixture of Zeotile phases (Zeotile-1, -2, and -3) is observed in Sample B (Fig.2). The predominating Zeotile-2 phase is built from the same double nanoslabs as in Zeotile-1, but has centred orthorhombic symmetry (Fig.2b). Zeotile-3,

occasionally detected with HREM (Fig.2c), has a tetragonal tiling pattern of the original single nanoslabs, measuring $1.3 \times 2.0 \times 4.0 \text{ nm}^3$.

A further preparation (Sample C) under acidic conditions yields pure Zeotile-4 (Fig.3a). The preparation starts from large nanoslabs with dimensions of $1.3 \times 8.0 \times 4.0 \text{ nm}^3$, obtained through acidification of nanoslab suspension. Triblock copolymer serves as tiling agent. Triblock copolymers of the Pluronics type are typically used in the synthesis of thick-walled, wide pore silica materials.³ The TPA and copolymer are evacuated from the solid material through calcination. Zeotile-4 is made up from stapled large nanoslabs arranged in a hexagonal appearing tile (Fig.3). The large nanoslabs used as building units are clearly visible in the micrograph (Fig.3).

In HREM, the tiling patterns show a high perfection throughout the individual Zeotile particles reaching micrometer sizes. The fine structure *within* a nanoslab however could not be resolved with HREM because of electron irradiation damage of the weak Si-O bonds. The Fourier transform of the HREM images only shows information on the nanoslab tiling; no reflections related to the internal nanoslab structure are detected. Also XRD does not reveal internal slab information. Individual, dispersed nanoslabs, because of their small size, do not give rise to Bragg type diffraction related to their internal structure.⁵ In the Zeotiles, slight misalignments in the tiling prevent the manifestation of this Bragg scattering.

The integrity of the Silicalite-1 building blocks in the Zeotiles however is confirmed with ^{29}Si MAS NMR, showing the unique silicon connectivity of the nanoslabs to be maintained during the tiling and the template evacuation. In addition, nitrogen adsorption isotherms at -196°C and alkane separation experiments confirm the presence of Silicalite-1 microporosity next to mesopores with precise diameters (3.2 nm, 3.1 nm and 9.4 nm for Zeotile-1, -2 and -4, respectively, as derived from the nitrogen adsorption isotherms).

Zeotiles are unexpectedly robust materials combining the advantages of micro- and mesoporous silicate structures. The four prepared Zeotiles illustrate the structural diversity of the material. From a structural point of view, other combinations are equally possible. At the first level, nanoslabs with alternative framework types can be used, and heteroatoms incorporated. At the second levels, the tiling pattern can be altered by changing the nature of the structure-giving agent and the synthesis conditions (concentration nanoslabs, composition nanoslabs, concentration structure giving agent, temperature). Therefore, it is expected that new members of the Zeotile material family will be prepared and identified in the near future.

Methods

Silicalite-1 nanoslab suspension. Nanoslabs were prepared from 37.32 g TEOS (Acros, 98%) hydrolysed in 32.13 g aqueous TPAOH solution (Alfa, 40 wt.-%) under stirring. After hydrolysis, 30.55 g water was added and stirring continued for 24 h.

Sample A (Zeotile-1). 60 g of a 10 wt.-% aqueous CTAB (Acros, 99%) solution heated at 80°C was combined with 20 g nanoslab suspension under stirring; stirring continued for 20 minutes, where after the precipitate was recovered by filtration, washed with water and dried at 60°C for 2 days. The organic templates were removed by slurring 3 g of the solid in 200 mL ethanol containing 0.02 mol nitric acid at 77°C for 1 h. The solid was recovered by filtration and washed with ethanol. The oxidation with nitric acid was repeated twice. The sample was finally dried at 60°C overnight.

Sample B (mixture of Zeotile-1, -2, and -3). 6 g of CTAB was slowly added to 20 g nanoslab suspension under vigorous stirring. The slurry was stirred for 24 h and subsequently heated at 90°C for 4 days under quiescent conditions. The precipitate was recovered and treated the same way as Sample A.

Sample C (Zeolite-4). 10 g of pluronic P123 triblock copolymer from BASF ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) was dissolved in 90 g water under stirring. An amount of 24 g of this template solution was combined with 8 g of 5 M HCl aqueous solution. 18 g of nanoslab suspension was slowly combined with another 9 g 5 M HCl solution under vigorous stirring and finally combined with the acidic triblock copolymer solution. The mixture was heated at 90°C under quiescent conditions during 4 days. A solid product was formed and separated from the liquid by centrifugation at 12,000 rpm. The product was washed with water until the pH exceeded the value of 3. The sample was dried at 60°C, and finally calcined at 350°C with a temperature ramping of 0.5°C/min.

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CLAIMS

1. Crystalline silica material comprising nanoslabs characterised in that the material has two levels of porosity and structural order.
2. Crystalline silica material according to claim 1 wherein the first level building units are nanoslabs and at the second structural level, nanoslabs are linked through their comers, edges or faces following patterns imposed by interaction with cationic surfactant or triblock copolymer molecules.
3. Crystalline silica material according to claims 1 and 2 wherein the nanoslabs are uniform size nanoslabs having the Silicalite-1 zeolite framework.
4. The use of cationic surfactants or triblock copolymer molecules to impose a structural organisation to the nanoslabs.

ABSTRACT

The present invention describes a new class of crystalline silica materials, said materials having two levels of porosity and structural order. At the first level, building units are nanoslabs of uniform size having the Silicalite-1 zeolite framework generated by the tetrapropylammonium template.⁵ At the second structural level, nanoslabs are linked through their corners, edges or faces following patterns imposed by interaction with cationic surfactant or triblock copolymer molecules. After evacuation of the organic molecules, microporosity is obtained *inside* the nanoslabs, and a precise mesoporosity *between* the nanoslabs depending on the tiling pattern of the zeolite slabs. Therefore, the use of cationic surfactants (preferably quaternary ammonium salts) or triblock copolymer molecules in order to impose an organisation to the nanoslabs is a second object of the invention. In a first embodiment four different tiling patterns were prepared and directly imaged by electron microscopy. X-ray diffraction confirms the mosaic structures derived from electron microscopy. Application fields are catalysis and molecular separation, adsorption of metal ions, fixation of biologically active species, electro-optical and dielectric materials.

